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Research Article

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Novel optimization technique to determine polarization characteristics of a corroding metal

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Abstract: Polarization data characterize the corrosion behavior of a metal giving a quick estimate of corrosion current density i_{corr} and corrosion potential E_{corr}. These two characteristics determine the corrosion rate and position of the metal in galvanic series. The chosen system for the study is steel (SS304) in NaCl solution. In these studies, i_{corr} and E_{corr} of Butler-Volmer equation are obtained by fitting the full expression to experimental current vs potential data unlike the graphical method using Tafel-slopes. MATLAB optimization tool box is utilized for this purpose. The novel optimization technique is explained for determining E_{corr} and i_{corr}

Keywords: Polarization; Butler-Volmer equation; Optimization

1 Introduction

The corrosion rate of any metal sample in a given electrolyte solution can be estimated in two ways: long term gravimetric or weight loss studies and short term polarization characterization using electro-chemical workstation.

Generally gravimetric studies or weight loss studies through immersion experiments will take longer time of nearly 3 to 6 months to find out the corrosion rate of a metal sample in terms of *mmpy* (millimeters per year). On the other hand polarization studies using an electrochemical workstation will give the corrosion potential (E_{corr} in V) and corrosion current (i_{corr} in A/cm^2) values in a short time less than 1 to 2 hours. i_{corr} is useful to calculate the corrosion rate in *mmpy* of the metal sample by multiplying with appropriate factor. E_{corr} is useful to identify whether the metal will corrode preferentially or not when it is in combination with another metal forming a galvanic couple.

In literature, the electrochemical behavior of type 304 stainless steel was investigated in presence of alkaline environments of different pH to know the susceptibility in concrete structures [1]. Polarization studies on pipeline steel subjected to acidic environment were performed to study the polarization characteristics at various immersion times [2]. Microscale corrosion study was carried out and compared with conventional electrochemical technique for 304L stainless steel in NaCl solution [3]. The stability of passive layers on stainless steel 304 was studied using electrochemical noise measurements [4]. The polarization tests provide the corrosion characteristics of a metal. Although it is a quick test there are certain areas of ambiguity in selecting pre-immersion times and potentiodynamic scan rates and extrapolation of Tafel-slopes for finding i_{corr} and E_{corr} [5–8]. An alternative curve fitting method is developed in this paper to obtain the four parameters of Butler-Volmer expression [9]. Results from the latter method are compared with experimental polarization data for validation through error analysis.

2 Experimental

2.1 Materials and sample preparation

Stainless steel samples of type 304 were used in this study in the form of coupons of size 25 mm × 25 mm and thickness 4 mm. Sample surfaces were polished using emery papers of grades 320, 1000, 1200, 1500, 3000 and 4/0 and wet polished with alumina powder, cleaned with water, alcohol and dried in hot air to get smooth and mirror finish (Figure 1(a)). NaCl electrolyte solution of concentration 16 g/l is prepared. Moreover this electrolyte corresponds to half of sea water concentration. It was chosen so that it has utility for marine application studies.

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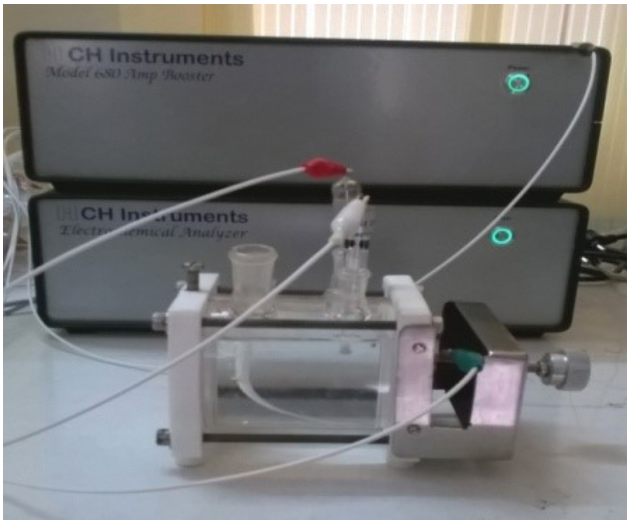
(a)



(b)

Figure 1: (a) Polished metal specimen. (b) Flat corrosion cell.

2.2 Polarization studies

A flat corrosion cell (Figure 1(b)) is used which consists of a horizontal glass cylinder carrying NaCl solution, a port for reference electrode, counter electrode and a holder for metal specimen as working electrode.

The electrochemical workstation is of CH Instruments, USA. The counter electrode is made of platinum and the reference electrode is a saturated calomel electrode (SCE). The metal sample is held in the working electrode port with an exposure area of 1 cm diameter (0.785 cm^2 area). After fixing the metal sample, the flat cell is filled with NaCl solution. The samples in combination with the electrolyte are held in contact for nearly zero immersion time. First, open circuit potential is determined by running the test for 10 minutes. The determined open circuit potential (OCP) is taken as reference and a Tafel-test from the software of the instrument is run for a range of potentials between 0.25 V below the OCP and 0.25 V above the OCP. The applied potential scan rate is 0.2 mV/s and the I vs E data are acquired. The software associated with the electrochemical workstation plots I vs E data and saves to a file where I is the current in Amperes and E is the applied potential with reference to a reference electrode (SCE) in Volts. The obtained current, I is divided with surface area of the sample to obtain current density, i. The surface area of the sample is 0.785 cm^2 since it is in a circular shape of 1cm diameter. The resultant current density vs applied relative potential is represented as potentiodynamic polarization curve of type 304 stainless steel measured at room temperature in 16 g/l NaCl solution is shown in Figure 2.

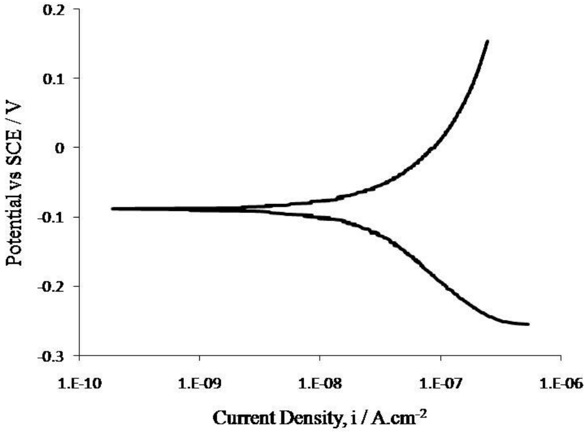


Figure 2: Polarization curve of SS304 in 16 g/l NaCl solution.

3 Optimization model using Butler-Volmer equation

3.1 Model description

In graphical method of obtaining Tafel-slopes, there are certain areas of ambiguity upon where to draw the tangents to find the slopes of cathodic and anodic parts of polarization curve (Figure 2). The general form of Butler-Volmer equation pertaining to corrosion current vs applied potential is represented in Eq. (1a) [10]. For our purpose, the temperature is constant for all experiments and concentration variations are assumed negligible. This assumption leads to a simplified or modified Butler-Volmer

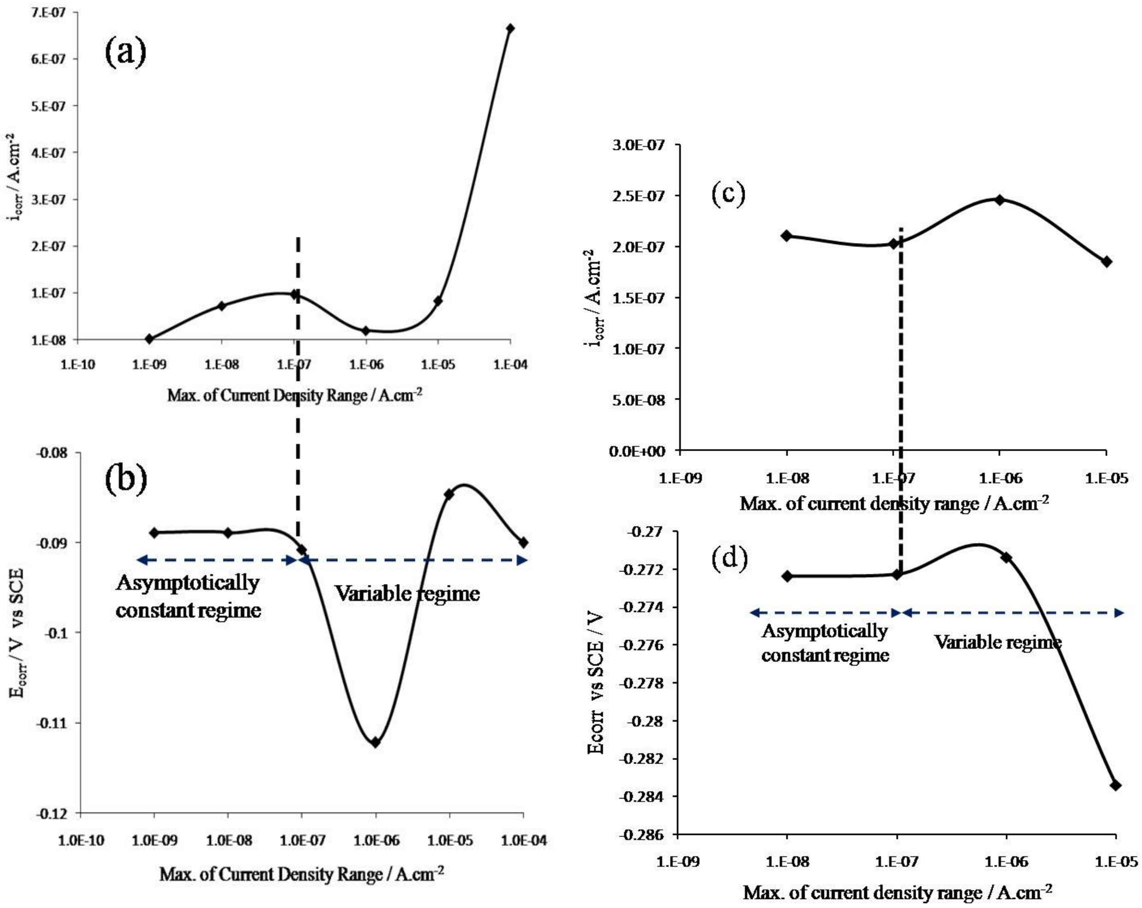


Figure 3: Graphical method of identifying the E_{corr} and i_{corr} from the polarization data (a) i_{corr} vs current density range for SS304. (b) E_{corr} vs current density range for SS304. (c) i_{corr} vs current density range for SS316. (d) E_{corr} vs current density range for SS316.

equation as in Eq. (1b).

$$i = i_0 \left\{ \frac{C_R(0,t)}{C_R^b} e^{\frac{(E-E_0)}{b_a}} - \frac{C_0(0,t)}{C_0^b} e^{\frac{-(E-E_0)}{b_c}} \right\} \tag{1a}$$

$$i = i_{corr} \left(e^{\alpha(E-E_{corr})} - e^{-\beta(E-E_{corr})} \right) \tag{1b}$$

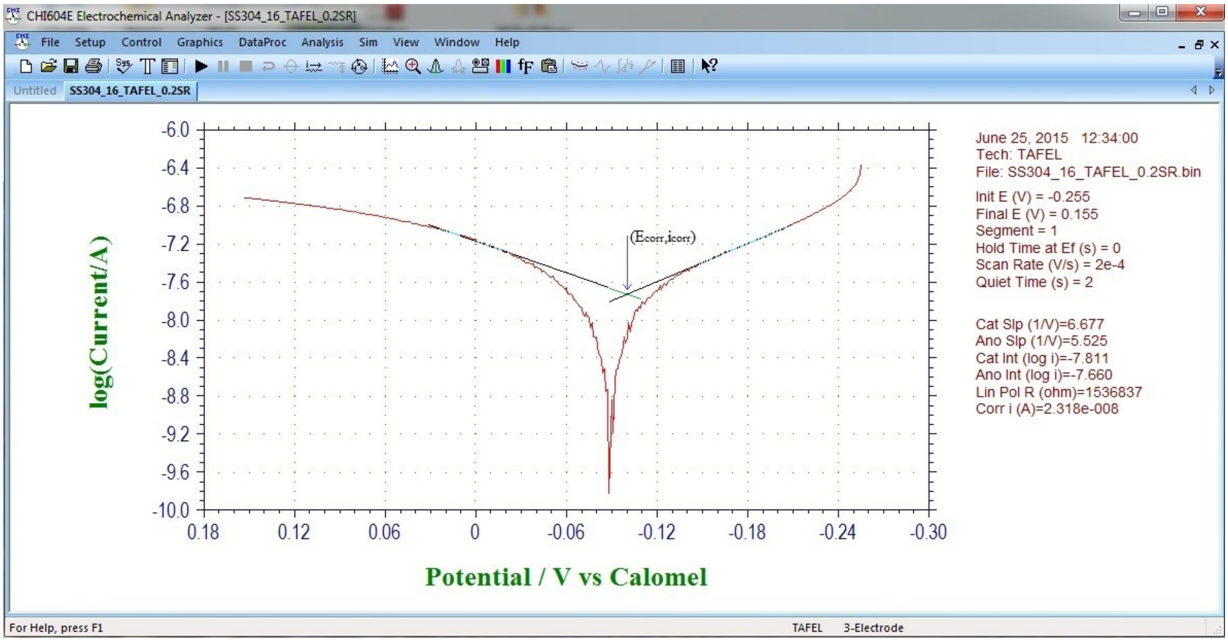
A new optimization technique is used to fit the four parameter modified Butler-Volmer equation in Eq. (1b) to calculate the polarization parameters using the experimentally obtained polarization data. It has four parameters to be determined: E_{corr}, i_{corr}, α and β. The parameters are found by optimization technique where the error between experimental data and prediction of Eq. (1b) should be minimized.

The error or the objective function is defined in Eq. (2). It is equal to the standard deviation between the predicted current of equation Eq. (1b) and the experimental current data at each of the potentials applied.

$$\text{Error} = \sqrt{\frac{\sum \left(i_{pred} - i_{expt}\right)^2}{n-1}} \tag{2}$$

where, n is the number of data points. The chosen range of current density is of equal magnitude both on cathodic and anodic side of the polarization data. In MATLAB software *fminsearch* subroutine is utilized in finding the optimum values of E_{corr}, i_{corr}, α and β such that the error is minimized.

The range of current data to be included in evaluating the error in Eq. (2) is also a matter of choice. Hence various limits of the current density range for SS304 in 16 g/l NaCl solution are taken and the corresponding optimum values of the four parameters are found. The obtained optimum i_{corr} values as a function of these limits are plotted (Figure 3(a)). Similarly, the obtained optimum E_{corr} values are plotted (Figure 3(b)). Similarly, for SS316 in 35 g/l NaCl solution, the obtained optimum i_{corr} values as a function of the limits of current density range (Figure 3(c)) and optimum E_{corr} values are plotted (Figure 3(d)).

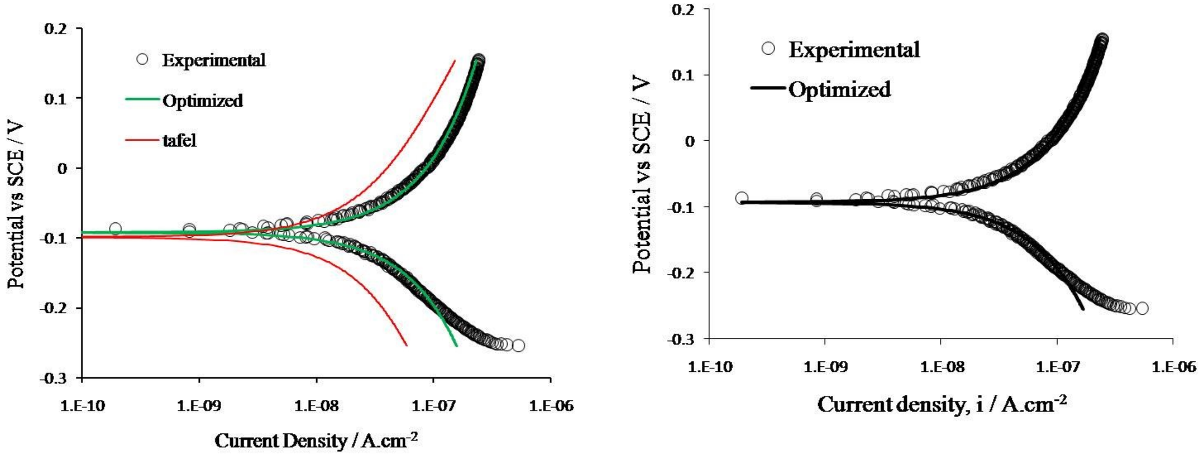


June 25, 2015 12:34:00
Tech: TAFEL
File: SS304_16_TAFEL_0.2SR.bin

Init E (V) = -0.255
Final E (V) = 0.155
Segment = 1
Hold Time at Ef (s) = 0
Scan Rate (V/s) = 2e-4
Quiet Time (s) = 2

Cat Slp (1/V)=6.677
Ano Slp (1/V)=5.525
Cat Int (log i)=-7.811
Ano Int (log i)=-7.660
Lin Pol R (ohm)=1536837
Corr i (A)=2.318e-008

(a)



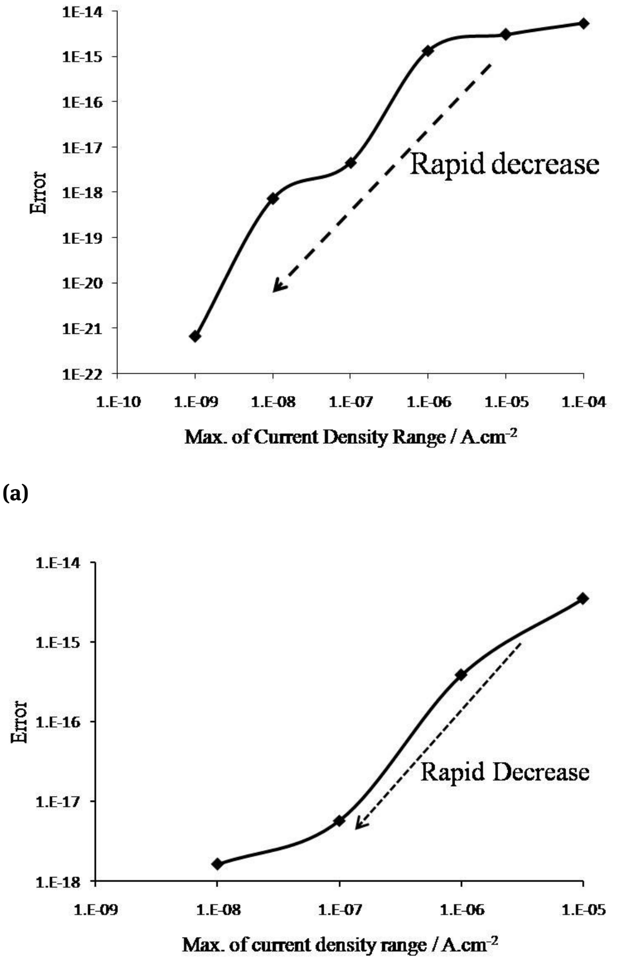
(b) **(c)**

Figure 4: (a) Tafel extrapolation using the software (b) Comparison of polarization data from experiments with curve obtained from Tafel slopes and the curve obtained from optimized parameters in B-V expression (c) Comparison of experimental and fitted polarization curves for SS304 in 16 g/l NaCl solution.

3.2 Model Validation

The entire predicted B-V-curve for SS304 in 16 g/l NaCl solution is shown along with the experimental values of current density vs potential in Figure 4(c). It can be noticed that the error is very small as observed visually in Figure 4(c). The quantified error is also presented in Figure 5(a) and Figure 5(b) for various values of current density ranges and for two different types of steel alloys in different concentrations of electrolyte solution.

An in depth analysis is carried out on the usage of Tafel-slopes method versus our proposed method in determining the exponential constants/parameters in B-V equation. In order to check the applicability of Tafel-slopes the E vs log (i) data is analyzed. The derivative of E with respect to log (i) has to be constant over a range of at least one decade in current density i in order to utilize the Tafel-slopes method. This particular derivative is evaluated and plotted in Figure 6 for SS 304 subjected to polarization in NaCl electrolyte solution of 16 g/l concentration.



(a)

(b)

Figure 5: Error between predicted and experimental current density data as obtained from the present optimization technique for (a) SS304 in 16 g/l NaCl solution (b) SS316 in 35 g/l NaCl solution.

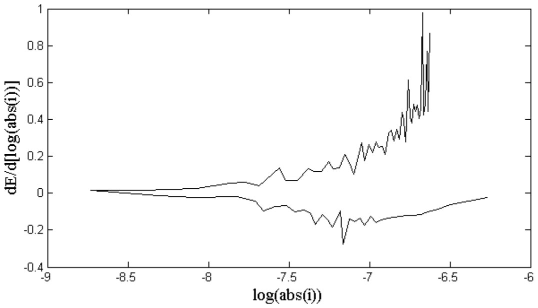


Figure 6: The local slope of *E* vs log (*i*) curve for SS304 in 16 g/l NaCl solution.

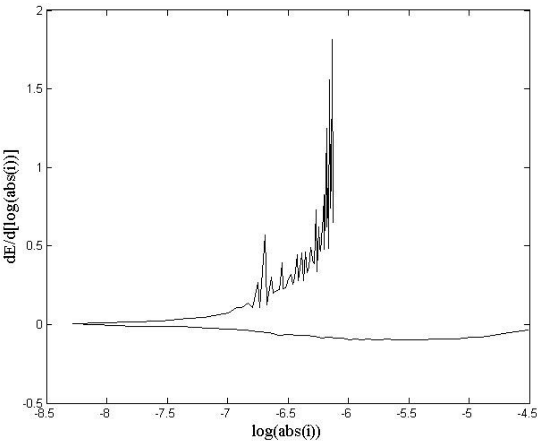


Figure 7: The local slopes of *E* vs log (*i*) curve for SS316 in 35 g/l NaCl solution.

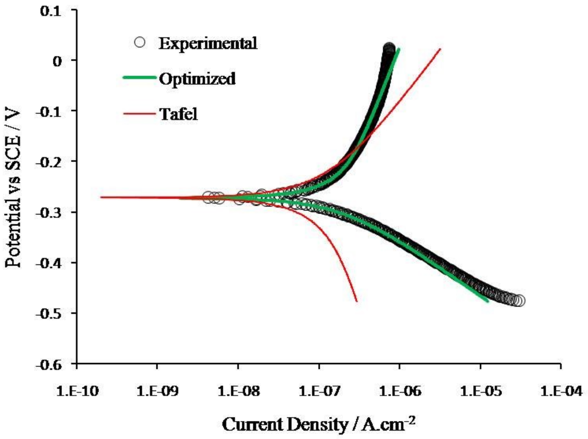


Figure 8: Comparison of polarization data from experiments with curve obtained from Tafel slopes and the curve obtained from optimized parameters in B-V expression for SS316 in 35 g/l NaCl solution.

It can be noticed that the slope is somewhat constant on cathodic side. On the anodic side the slope value is not constant even for one decade change in the corrosion current density which is a requirement for using Tafel-slopes method. Because of this partial suitability of Tafel-slope concept, the parameters of B-V expression cannot be obtained by geometric approach of drawing a slope at some location of *E* vs log (*i*) curve. Such ambiguity and non-constancy of the slopes is also demonstrated after analyzing the *E* vs log (*i*) curve of SS316 is as shown in Figure 7.

Hence our proposed approach of utilizing multi-parameter optimization technique through contemporary computational software such as MATLAB is justified. The purpose of proposing a new approach is to have an accurate representation of B-V expression for simulating galvanic corrosion in the case of bi-metallic joints and micro-galvanic corrosion/intergranular corrosion in the case of dual phase alloys.

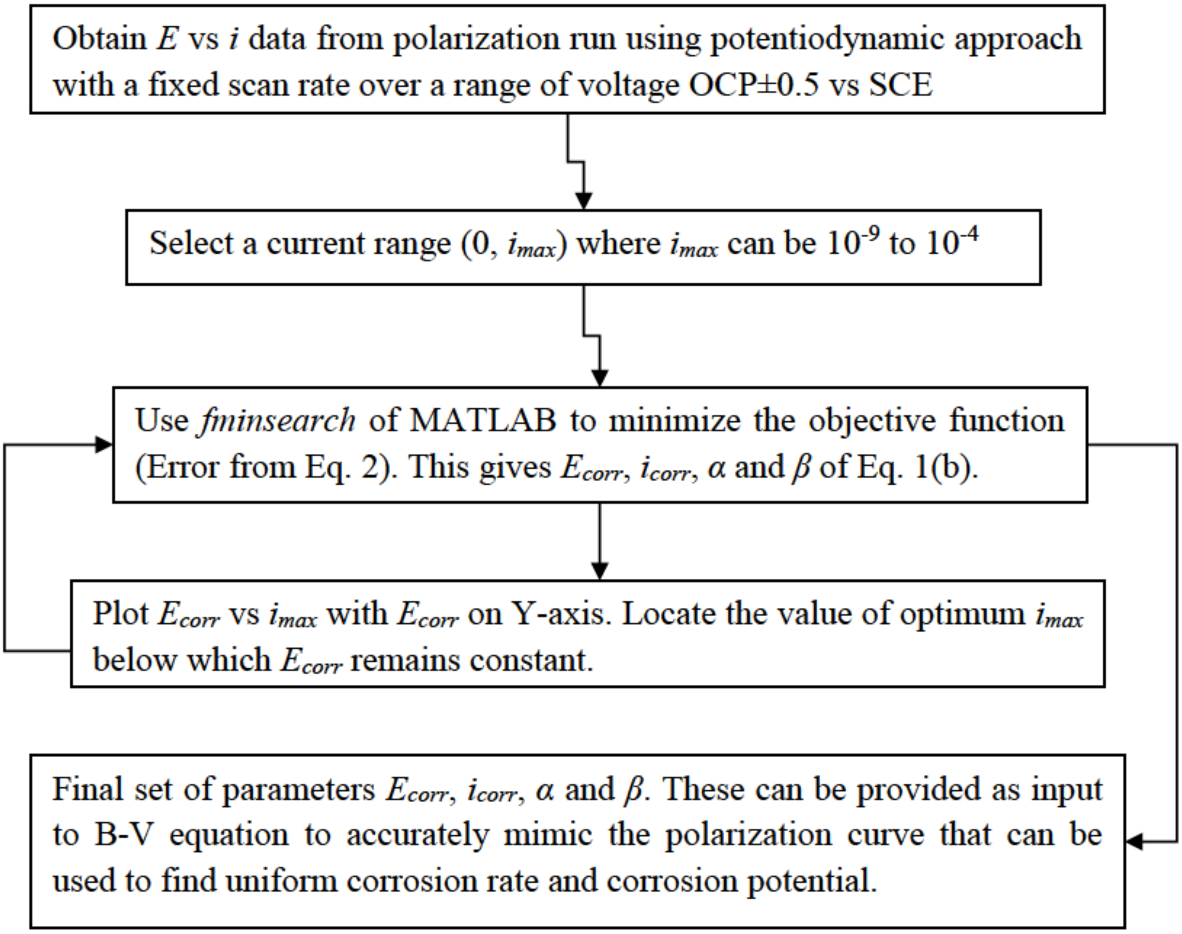


Figure 9: Algorithm to determine polarization characteristics from potentiodynamic data of a metal in a given electrolyte as per the present proposed method.

To provide evidence that the present proposed method of determining B-V equation parameters the E vs log(i) curve from experiment is superior, Tafel-method and the present optimization method are presented in Figure 4(b) and Figure 8 for two different metals corroding in NaCl solution.

4 Discussion

To summarize the steps followed in determining the four parameters of B-V equation Eq. (1b) the following algorithm is presented in Figure 9.

A number of hurdles were encountered in the form of multiple answers for the parameters of Butler-Volmer equation Eq. (1b) during optimization. To consider feasible values of parameters, α and β have to be positive and E_{corr} should be close to the voltage where the current goes to least possible value or changes its sign from negative to positive.

After an in depth analysis of predicted optimum E_{corr} (Figure 3(b)), it can be deduced that there are two distinct regimes. There is a variable regime where predicted E_{corr} is changing as the current density range is also changed. This again is an ambiguity similar to Tafel method. But for a critical current density of around 10^{-7} A/cm^2 and below E_{corr} remains asymptotically constant at –0.09 vs SCE, V (approx.). Hence it can be called an asymptotically constant regime. It can be noticed that as the maximum of the upper limit of current density range used for optimization is reduced then the predicted i_{corr} approaches zero as in Figure 3(a). This is true because exactly at E_{corr} the corrosion current is zero owing to equal magnitude of anodic and cathodic currents by definition. Now it is proposed that the dotted line (Figure 3(a) and Figure 3(b)) where the E_{corr} value starts to be asymptotically constant can be taken as the optimum upper limit of current density range

Table 1: B-V expression parameters from two different methods for SS304 in 16 g/l NaCl electrolyte solution

Method	E_{corr}, V vs SCE	i_{corr}, μA/cm^2	α, V^{-1}	β, V^{-1}	Error
Tafel	−0.0991	0.02953	6.677	5.525	8.6514E−08
Optimization	−0.0901	0.31359	1.3996	1.6078	3.82838E−08

Table 2: B-V expression parameters from two different methods for SS316 in 35 g/l NaCl electrolyte solution

Method	E_{corr}, V vs SCE	i_{corr}, μA/cm^2	α, V^{-1}	β, V^{-1}	Error
Tafel	−0.2711	0.1344	10.818	4.071	4.51912E−06
Optimization	−0.2719	0.1373	8.4526	24.8563	1.96421E−06

to be used for determining i_{corr}. The lower limit is negative of the previously mentioned upper limit. Corresponding to these limits of range of potential vs current density i_{corr} is found as $3.1359 \cdot 10^{-7}$ A/cm^2 for SS304 in 16 g/l NaCl electrolyte solution. The four parameters of B-V expression as in Eq. (1b) are listed in Table 1 and Table 2 for two different alloys of steel. It can be noticed that the error using the present method is much less as compared to Tafel-slopes method. The error in the last column is evaluated using the stated equation Eq. (2). The difference between i_{corr}, from Tafel method and present optimization method is less at higher concentrations possibly owing to nearly constant value of the i vs V slope over a larger span of current density as also found in Figure 6 and Figure 7. Another factor could be the higher conductance and less fluctuation in current density measured for higher concentration of electrolyte solution although the two samples are of slightly different composition as SS304 and SS316 with both metals having austenite phase. Thus a novel optimization technique is developed for determination of E_{corr} and i_{corr} from polarization data.

5 Conclusions

The *i-V* characteristics of a corroding metal such as SS304 in NaCl solution are modeled by Butler-Volmer equation represented by a four parameter expression. These four parameters are determined by numerical optimization using *fminsearch* of MATLAB. The standard deviation between predicted current density and experimental values at all applied potentials is taken as the error for minimizing using optimization technique. It gave rise to a few multiple answers but the requirement that the exponential coefficients α and β to be positive have zeroed onto a single set of optimum parameters for a given metal-electrolyte combination. It was demonstrated successfully that Butler-Volmer equation fits the experimental *i-V* data. It was demonstrated that there is an asymptotically constant regime of E_{corr} values depending on the maximum current density range used in optimization process. The identification of suitable current density range to be used for determining the optimum i_{corr} and E_{corr} is established. Thus a novel analysis technique is developed for determination of polarization characteristics of a corroding metal.

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